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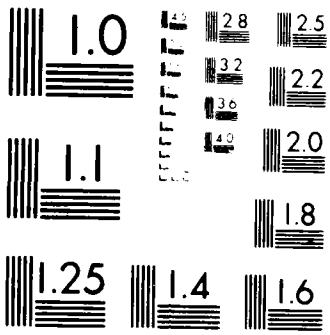
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Room temperature Raman microprobe x-ray diffraction and electrical resistivity measurements have been performed on carbon/carbon composites made from mesophase pitch which were heat treated at temperatures above 2680 Celsius. Results of these measurements indicate that both the ex-pitch carbon fiber and mesophase pitch matrix constituents of the composites were highly graphitic, exhibiting in-plane crystallite dimensions greater than 1000 Angstroms. The c-axis crystallite dimensions were determined by analysis of x-ray diffraction peak widths to be approximately 150 Angstroms. Copper chloride was successfully reacted with these carbon-carbon composites forming a stage three graphite intercalation compound in both the fibers and the matrix, as determined by their Raman spectra.

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Electronic and Structural Studies of Carbon/Carbon Composites

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Abstract

Room temperature Raman microprobe, (00ℓ) x-ray diffraction and electrical resistivity measurements have been performed on carbon/carbon composites made from mesophase pitch which were heat treated (T_{HT}) at 2680°C, 2820°C and 3015°C. Results of these measurements indicate that both the ex-pitch carbon fiber and mesophase pitch matrix constituents of the composites were highly graphitic, exhibiting in-plane crystallite dimensions (L_a) greater than 1000 Å for this range of T_{HT} values. The c-axis crystallite dimensions (L_c) were determined by analysis of x-ray diffraction peak widths to be $\sim$ 150Å. $CuCl_2$ was successfully reacted with T_{HT} = 3020°C composites forming a stage 3 intercalation compound in both the fibers and the matrix, as determined by their Raman spectra.

1 Introduction

High temperature strength, durability and light weight are several of the properties which have spawned a great deal of interest in carbon/carbon (C/C) composites. Originally manufactured for the aerospace industry, these materials are now found in virtually all areas of technology in which the above properties are important. As the number of applications grows, it becomes imperative to understand the physical properties of these important and interesting materials. Since the phrase *carbon/carbon composite* covers a very large range of materials, we have restricted our research to the particular type of composite that is composed of layers of two dimensionally woven carbon fibers impregnated by a mesophase pitch binder (matrix). The composites were heat treated at high temperatures ($T_{HT} > 2500$°C) in order to graphitize the fibers and the matrix. Different types or preparations of C/C composites used in other studies include three dimensional fiber weaves [1], chemical vapor deposition [2], plasma etched CVD [3] and carbon fiber–epoxy materials [4]. A recent review of C/C composites has been given by Fritz *et al.* [5].

Previous studies have shown Raman scattering to be a useful, nondestructive probe of the graphitization of C/C composites [6,7,8]. In this study, we have used a Raman microprobe to examine the graphitic characteristics of the heat treated carbon fibers and the matrix independently. Analysis of the Raman microprobe spectra and (00ℓ) x-ray diffraction peak widths yields approximate values of L_a and L_c, the in-plane and c-axis crystallite dimensions, respectively [9].

The graphitization of the composites was also investigated by measuring the room temperature electrical resistivity parallel ($\rho_{\parallel}$) and perpendicular ($\rho_{\perp}$) to the plane of the fiber weave. The electrical anisotropy ($\rho_{\perp}/\rho_{\parallel}$) in conjunction with the basal plane crystallite dimension (L_a) provided qualitative information concerning the random orientation of the graphitic crystallites in the matrix with respect to the plane of the woven fibers.

The applicability of carbon/carbon composites to science and technology renders the study of intercalation effects on the electronic and structural properties of these materials more than academic. In this respect, we have reacted some of the samples with the compound $CuCl_2$. Metal chlorides are known to react with graphite to form acceptor-type graphite intercalation compounds (GICs) [9,10], and in particular the $CuCl_2$ compounds are technologically attractive because of their high electrical conductivity and air stability [9]. The same characterization methods employed in the study of the pristine (before reaction) composites (e.g. Raman microprobe, x-ray diffraction and electrical resistivity) were applied to the intercalated composites to investigate the effect of intercalation on the electronic and structural properties of the carbon/carbon composites.

2 Experimental Details

Commercially available carbon fibers (Amoco P-100) and mesophase pitch (Ashland Oil A-240) were chosen as the constituents for the composite materials because of their ability to graphitize at heat treatment temperatures (T_{HT}) above 2000°C [11]. The fibers were woven two dimensionally and then impregnated by the pitch using standard techniques [12]. Layers of the impregnated weave were stacked and hot pressed under pressure forming plates with approximate dimensions $3 \times 5 \times 0.5$ cm^3. Samples were heat treated at several different temperatures (T_{HT} = 2680°C, 2820°C and 3015°C) for $\sim$ 30 minutes in a graphite tube furnace.

Raman scattering measurements were performed using a Raman microprobe system [13] with a spatial resolution of 1–2 μm. This resolution enabled us to separately examine the Raman spectra of the carbon fibers and the matrix.

Several pieces of the T_{HT} = 3015°C sample ($\sim 4 \times 4 \times 1$ mm^3) were placed in a quartz ampoule with anhydrous $CuCl_2$ (Aldrich Chemical Co., Gold Label) and sealed under several atmospheres pressure of Cl_2 gas. The ampoule was placed in a single zone furnace held constant at 550°C for $\sim$ 1 week. The reaction conditions employed in this work are not unique to the intercalation of metal chlorides into graphite. A recent paper by Meschi *et al.* [14] reviews in detail many publications concerning the intercalation conditions of metal chlorides into graphite fibers.

3 Results and Discussion

3.1 Carbon/Carbon Composites

The first order Raman microprobe spectra obtained from the carbon fibers and the matrix are shown in Figs. 1 and 2, respectively.

In the frequency range studied (1200 – 1800 cm^{-1}), Raman modes associated with the graphitic E_{2g_2} ($\sim$ 1585 cm^{-1}) and disorder-induced ($\sim$ 1360 cm^{-1}) phonons can be observed. Raman spectra of the carbon fibers (Fig. 1) and the matrix (Fig. 2) exhibit a very strong E_{2g_2} phonon mode and no evidence for a disorder-induced mode. The absence

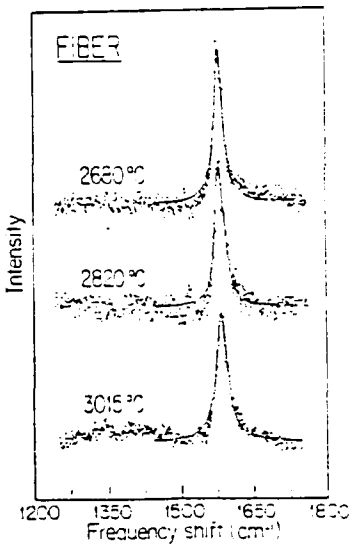

Figure 1: Raman spectra obtained from the fibers of the C/C composites for different heat treatment temperatures T_{HT}.

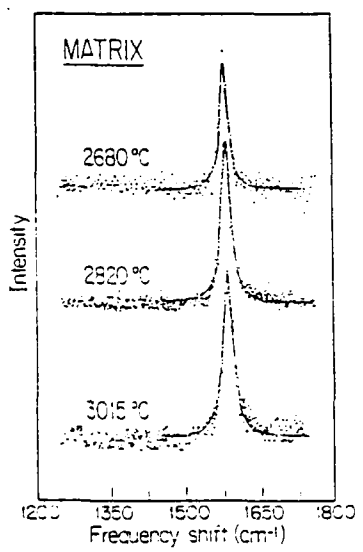

Figure 2: Raman spectra obtained from the matrix of the C/C composites for different heat treatment temperatures T_{HT}.

of the disorder-induced mode in these spectra indicates that the carbon fiber and matrix constituents of the composites are highly graphitic for $T_{HT} \geq 2680°$. Least square fits of Lorentzian lineshapes to the data are displayed as solid lines in the figures. Numerical results for these Lorentzian fits (the center frequency ω and the peak width at half maximum intensity Γ) are given in Table 1. The absence of a disorder-induced mode in these spectra implies large in-plane crystallite sizes ($L_a \geq 1000$ Å) for both the matrix and the fibers [15].

The frequency shift ω and the peak width Γ of the E_{2g_2} graphitic phonon are sensitive to disorder [15,16], which causes this line to broaden and shift to higher frequency, reflecting a high density of phonon states near 1620 cm^{-1} [16]. While contributions from the 1620 cm^{-1} phonon modes can be observed in disordered graphite ($T_{HT} \leq 2000°C$), no spectral evidence for such modes is apparent in Figs. 1 and 2. As can be observed in Table 1, the frequencies of the graphitic phonons are within an experimental uncertainty (± 2 cm^{-1}) of the phonon frequency (1585 cm^{-1}) of highly oriented pyrolytic graphite (HOPG). The peak widths listed

T_{HT} °C	Composite Type	ω cm^{-1}	Γ cm^{-1}	L_a Å	B deg	L_c Å	$\rho_{\|}$ $\mu\Omega$cm	$\rho_{\perp}$ $\mu\Omega$cm	$(\rho_{\perp}/\rho_{\|})$
2680	fiber	1583	11	≥ 1000	.544	~ 150	1185	15590	13
	matrix	1583	12	≥ 1000					
2820	fiber	1583	11	≥ 1000	.560	~ 150	995	10695	11
	matrix	1584	12	≥ 1000					
3015	fiber	1583	11	≥ 1000	.560	~ 150	875	8670	10
	matrix	1583	12	≥ 1000					

Table 1: Results of Raman microprobe, (00ℓ) x-ray diffraction and room temperature resistivity experiments on the pristine carbon/carbon composites.

in Table 1 are slightly larger than found in HOPG, indicating L_a of the C/C composites is somewhat smaller than the in-plane crystallite dimension of HOPG (i.e. $\sim 10,000$ Å).

Interpretation of the peak widths (B) of the (002) x-ray reflections in the Scherrer equation provide values of $L_c \sim 150$ Å [17], and analysis of the peak spacings in the Bragg equation yield d-spacings approaching that of single crystal or pyrolytic graphite (d = 3.35 Å) [9,10]. Comparing these L_c values with the L_a values obtained from the Raman microprobe study above, we find $L_a \geq 6.7L_c$.

Room temperature resistivities of the composites were measured parallel ($\rho_\parallel$) and transverse ($\rho_\perp$) to the fiber weave are summarized in Table 1. The $\rho_\parallel$ values are dominated by the longitudinal resistivities of the carbon fibers and the resistivity of the matrix connecting adjacent fibers. $\rho_\parallel$ values were found to be approximately 5 times greater than values reported by Oshima *et al.* [18] for individual heat treated P-100 fibers (i.e. $\rho =$ 390, 225 and 190 $\mu\Omega$ cm for $T_{HT} =$ 2500°C, 2750°C and 3000°C, respectively). We believe the larger values of $\rho_\parallel$ to be a consequence of the sample composition and not fiber disorder, consistent with the results of the Raman microprobe study. Measurement of $\rho_\perp$ provided qualitative information concerning the graphitization of the matrix. The electrical anisotropy ratios ($\rho_\perp/\rho_\parallel$) range from 10–13 and depend weakly upon T_{HT}. Previous studies of the electrical anisotropy of carbon-based composites have reported $\rho_\perp$ to be 2–4 orders of magnitude larger than $\rho_\parallel$ [19]. Hsu [20] attributed these high values of the transverse resistivity to the morphology of the graphite fibers which requires that part of the transverse current travels along the high-resistivity c-axis direction of the crystallites. Assuming this to be the case, our low values of $\rho_\perp$ must arise from conduction associated with the crystallites of the matrix. Since L_a was measured to be large for the matrix (greater than 1000 Å), we would expect ($\rho_\perp/\rho_\parallel$) ~ 1 if the basal planes of the graphitic crystallites were aligned normal to and ($\rho_\perp/\rho_\parallel$) $\sim 10^2 - 10^4$ if the planes were oriented parallel to the fiber planes. The low anisotropy ratio however, suggests the alignment of the pitch binder crystallites is not completely random, a property which may be attributable to graphitic crystallite growth in the matrix nucleated by crystallites in the neighboring fibers [21].

3.2 Intercalated Composites

Raman microprobe spectra of the fibers and the matrix in the $CuCl_2$-reacted composites are shown in Fig. 3. Data are represented by dots and the solid lines are fits to the data for the parameters shown. Both spectra clearly display a Raman doublet, characteristic of a stage 3 or higher graphite intercalation compound [9]. The lower frequency phonon ($\omega_i = 1583$ cm^{-1}) is associated with interior carbon layer modes, while the higher frequency mode ($\omega_b = 1614$ cm^{-1}) arises from carbon bounding layers (i.e. those carbon layers adjacent to the intercalate layers) [9]. The frequencies ω_b and ω_i are known to be sensitive to the stage index (n) of the GIC, and the general relationships of ω_j (j = i, b) vs. 1/n for acceptor-type GICs are shown in Fig. 4. Our values of ω_i and ω_b are plotted in Fig. 4, indicating that the Raman spectra in Fig. 3 correspond to stage n=3. Comparison of the lineshape parameters associated with the fiber and matrix constituents of the composite indicate consistency in the ω_i and ω_b values. However the peak widths of the matrix modes were found to be $\sim 10 - 40\%$ larger than the corresponding fiber modes. The wider peaks of the Raman spectrum of the intercalated matrix suggest smaller crystallites are present in the matrix than in the fibers, but the disorder is not nearly enough to introduce a 1360 cm^{-1} Raman line.

The c-axis repeat distance (I_c) of the intercalated composites was determined by (00ℓ) x-ray diffraction to be ~ 16.05 Å which corresponds with a stage 3 $CuCl_2$-GIC. Diffraction

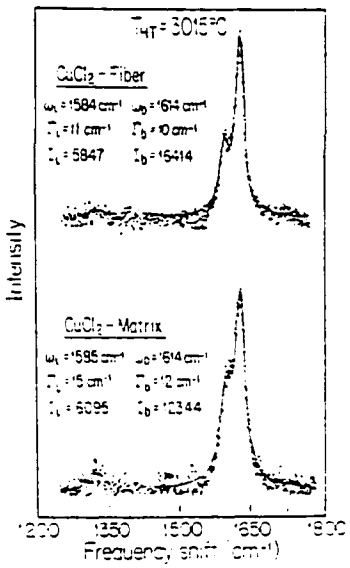

Figure 3: Raman spectra obtained from the fibers and the matrix of the $CuCl_2$ intercalated T_{HT} = 3015°C composite. Positions (ω), widths (HWHM, Γ) and the intensities (I) of the interior (i) and bounding (b) layer phonons are included.

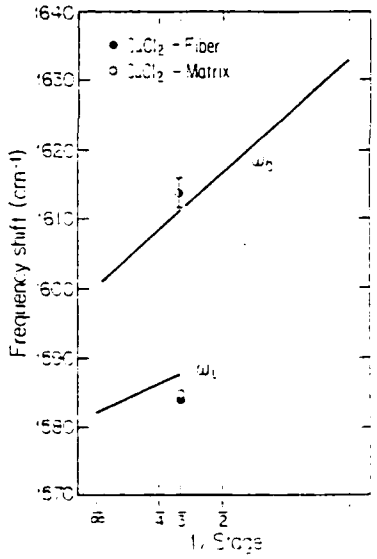

Figure 4: Frequency shift (ω) vs. reciprocal stage index (1/n) for acceptor–type GICs from Ref. [9]. ω values shown in Fig. 3 are plotted, and indicate the fibers and the matrix are stage 3 compounds. A typical error bar is shown.

peaks arising from higher stages may have been present: however, no graphitic reflections were observed, indicating that the intercalation was complete.

Resistivities ($\rho_{||}$ = 95$\mu\Omega$cm, $\rho_{\perp}$ = 855$\mu\Omega$cm) of the intercalated samples reflect an approximate 90% decrease in ρ from the pristine state, indicative of a metal chloride GIC, although $\rho_{||}$ was found to be ~ 6 times larger than reported values for $CuCl_2$ intercalated P–100 fibers ($\rho \sim 17\mu\Omega$cm) [18]. Intercalation did not significantly alter the electrical anisotropy relationship ($\rho_{\perp}/\rho_{||}$), demonstrating that intercalation reduced ρ for the matrix and fiber proportionately.

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